MAGNESIUM - Annual Survey covering the year 1979 *

Jean VILLIERAS

Laboratoire de Chimie Organique Physique, Faculté des Sciences de Nantes
2, rue de la Houssinière - 44072 NANTES Cédex
France

*Previous review see J. Organometal. Chem., 211(1981)1 - 175.

I. INTRODUCTION

Review articles published during 1979 concerned largely with Grignard reagents include :

- The annual survey covering the year 1977 by E.A. HILL [1].
- The synthesis of chiral tertiary alcohols by Grignard addition to glycosulose derivatives by J.C. FISCHER and D. HORTON [2].

Other reviews with a smaller content of organomagnesium chemistry have been published :

- Organometallics in Synthesis by D.J. THOMPSON and K.SMITH [3].
- Isocyanides in organic synthesis by M.P. PERIASAMY and H.M. WALBORSKY [4].

II. PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

A. Reaction of magnesium with organic halides

β-Bromoalkylamines, $R_2N-CH_2CH_2-Br$, reacted with highly activated magnesium between -75° and -100° in THF and ether to give Grignard compound 1 which decomposed between -50° and -20° by elimination of ethylene [5].

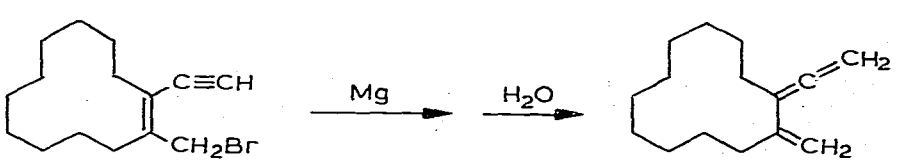
$$R_2N-CH_2-CH_2-Br + \text{Activated Mg} \xrightarrow[THF,\ Et_2O]{-75°,\ -100°} R_2N-CH_2CH_2-MgBr$$

1

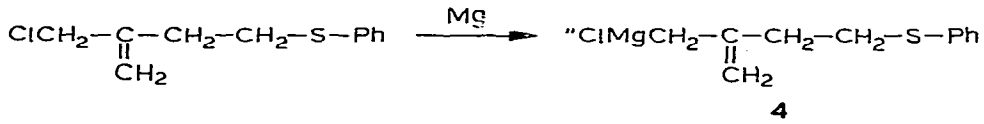
The thermal stability of 1 was found to increase in the sequence

$$R_2 = Ph, Me < Ph_2 < (C_6H_{11})_2$$

Various unsaturated Grignard reagents were prepared and used as synthetic reagents. They were obtained from several primary α-allenic bromides (e.g. $CH_2=C=CH-CH_2Br$) and their structure, stabilities and reactivities towards various halides were described [7]. The Cyclododecene derivative 2, on treatment with magnesium, followed by hydrolysis, gave the ene-allene-3 in 75% yield [8].



The sulfur-containing allylic Grignard reagent 4 was prepared and coupled geranyl chloride and isovaleraldehyde [9].



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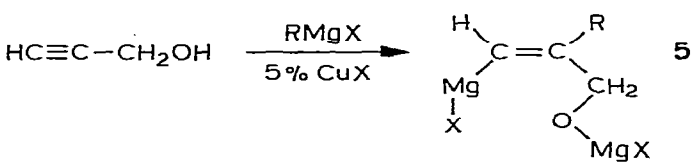
2-(2.6-Dichloroanilino)benzylbromide was obtained in THF from the parent benzylbromide and converted into 2-(2.6-dichloroanilino)phenylacetic acid [10].

B. Addition of Grignard reagents to multiple bonds

α-Acetylenic [11-13] and α-allenic [12,13] alcohols underwent regio- and stereospecific addition of Grignard reagents in the presence of cuprous halide, giving γ-functional vinylic magnesium compounds.



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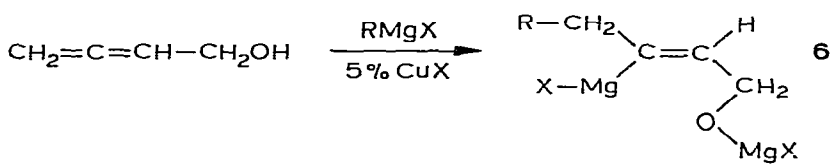

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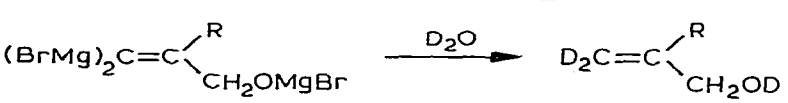
5 and 6 are valuable synthetic reagents for the stereospecific preparation of Δα,β-butenolides by carbonation, unsaturated ethers by coupling with aldehydes and ketones [11], vinyl iodides [13] by iodination.

Organomagnesium compounds add stereospecifically to metallated propargyl alcohols [14]. Thus $BrMg-C\equiv C-CH_2OMgBr$ reacts with RMgBr (R = Et, Ph, Allyl) containing 10% CuI to give 7.



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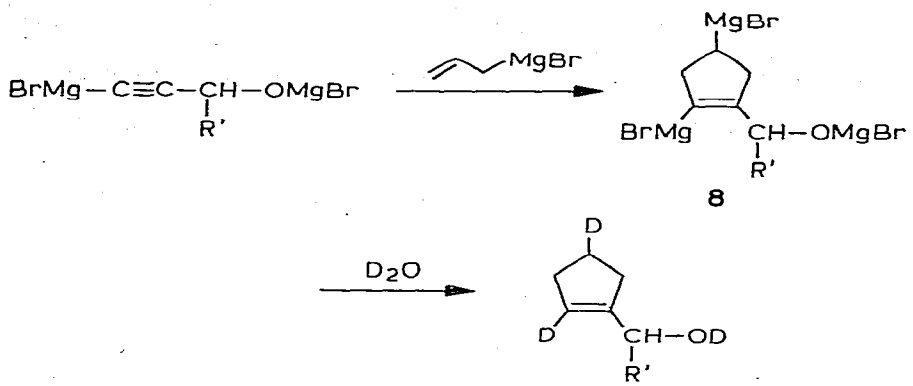
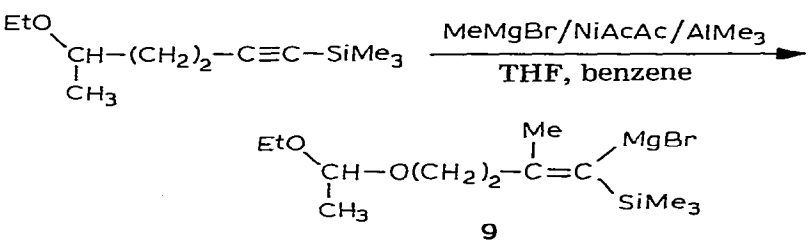
Cyclization and rearrangement occured wher $BrMg-C\equiv C-CHR'OMgBr$ was used in the presence of allylmagnesium bromide. It led to the formation of cyclopentenes 8 [14] which, on treatment with D_2O,



gave the tri deuterated cyclopentenyl carbinol.

The carbomagnesiation of 1,1-diphenylalkenols by various Grignard reagents (allyl, benzyl, terbutylmagnesium bromides) in diethyl ether was studied [131]. The stereochemistry of carbomagnesiation of 2-Cyclopentenols 3-Cyclopentenols, etc... with allyl magnesium bromide indicated that the accelerating and directing effect of the hydroxyl group on the reaction arose from the formation and intramolecular rearrangement of allyl magnesium alkoxides [132].

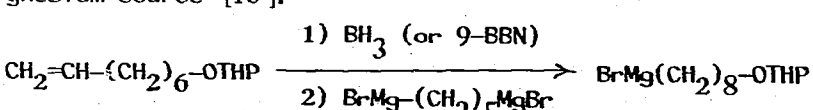
The nickel-catalyzed carbometallation of functionalized silylalkynes by Grignard reagents led to the formation of α-metallated silanes 9 [15] which were used in preparations of farnesol and geraniol



Z/E = 80-20 (in 4 hours)
= 15-85 (in 96 hours)

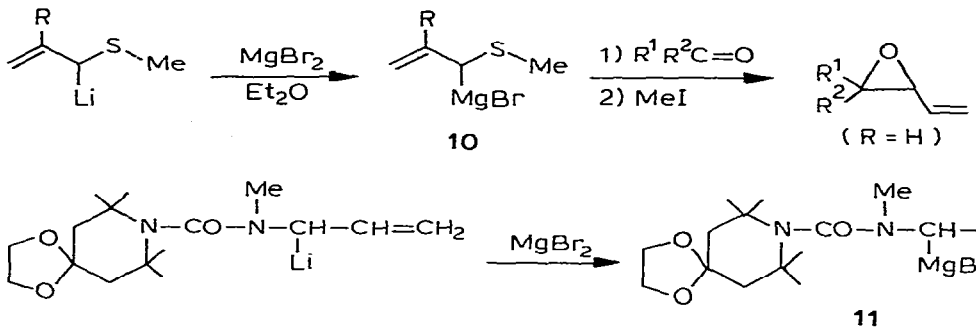
C. Formation of Grignard reagents by metal substitution

The selective transformation of organoboranes to Grignard reagents was performed using presence of pentane-1,5-di(magnesium bromide) as the magnesium source [16].

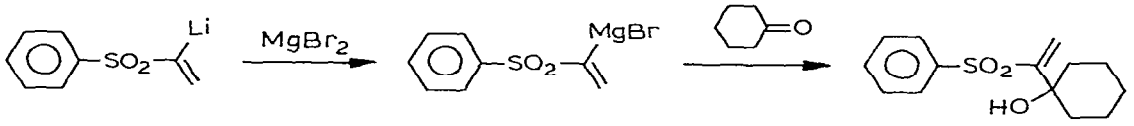


The Grignard intermediates were applied to the synthesis of pheromones.

Lithium-magnesium exchange was carried out with hetero substituted allyllithiums [17,18], giving the corresponding Grignard reagents 10 and 11 whose reactivities toward various electrophilic reagents were examined.



α-Lithiovinyl sulfones 28 also have been converted to the Grignard analogs in the same way [58]. The new organometallic reagent was shown to give better product yields than its lithio precursor in the coupling reaction with enolizable substrates.



D. Preparation of dialkyl- and diarylmagnesium reagents

The formation of di-n-butylmagnesium from n-butylmagnesium iodide in diethyl ether was achieved by addition of an excess of THF which served to precipitate MgI_2 - THF [19]. Bis [(trimethylsilyl)methyl] magnesium was obtained from $(Me_3Si)_2CHMgCl$ using 1,4-dioxane to precipitate the magnesium halide [20].

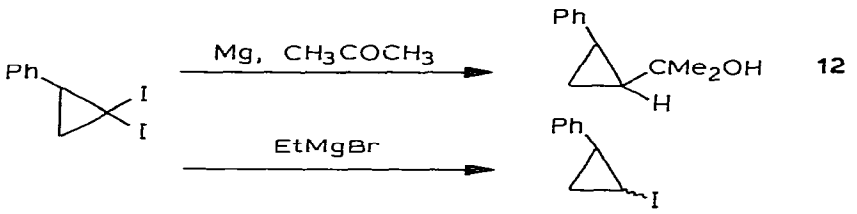
R_2Mg (R = Ph, $n\text{-}C_8H_{17}$, $n\text{-}C_6H_{13}$) were prepared by reaction of magnesium with RCl in the presence of R_2Mg and alkyl-aluminum halides, e.g., Bu_2AlCl [21]. Alkylaluminum-magnesium compounds $AlR_3/nMgR_2$ (R = C_5-C_{10} alkyl groups, n = 0.25 - 25) were prepared by the one-step reaction of magnesium and aluminum with RI in an hydrocarbon solvent at 40 - 110° [22].

References p. 39

E. Miscellaneous considerations on Grignard reagents

The preparation of aryl- and heteroaryltrimethylsilanes in 32 - 81% yield by "in situ" Grinard synthesis was performed by addition of aryl- and heteroaryl halides to magnesium and Me_3SiCl - HMPT with heating [23].

1,1-Diiodo-2-phenylcyclopropane underwent Grignard reaction with acetone to give 12 (with complete elimination of iodine) [24], while its reaction with EtMgBr gave chiefly 1-iodo-2-phenylcyclopropane isomers.



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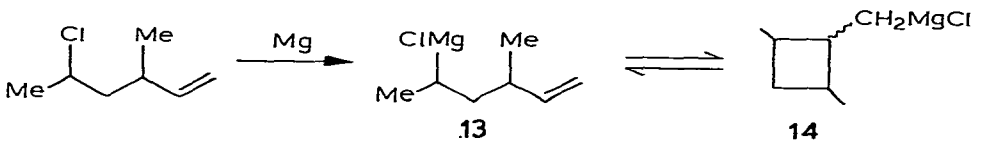
The reversible organomagnesium cyclization of the Grignard reagent from 5-chloro-3-methyl-1-hexene [25] has been studied.

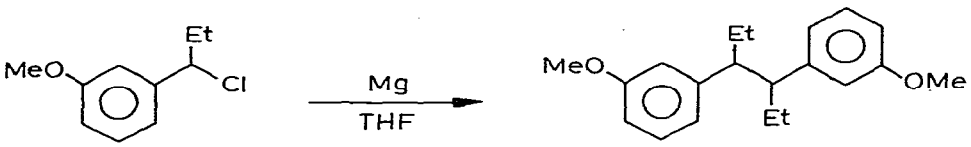


13 14

The factors with affect the equilibrium have been evaluated between 80° and 120°. Over this range the cyclic reagent is favored (14/13=3/1). The influence of methyl substitution in the destabilization of the organomagnesium function and the stabilization of the strained ring was discussed.

A considerable increase of the yield of Grignard reagents, together with a concurrent increase in the quantity of Wurtz reaction products, was found with 2-bromofluorene, 2-bromothiophene, chlorobenzene and diphenyl chloromethane when the reaction with magnesium is carried out in light [26]. With Ph_2CHCl the only isolated product was $Ph_2CH-CHPh_2$, while 2-bromofluorene gave 30 % 2-fluorenylmagnesium bromide in the presence of light and only a 12% yield in the dark.

Carbon–carbon coupling of 3-MeO-C_6H_4-CHCl-Et [27] with magnesium in THF gave diastereoisomeric diphenylhexanes 15



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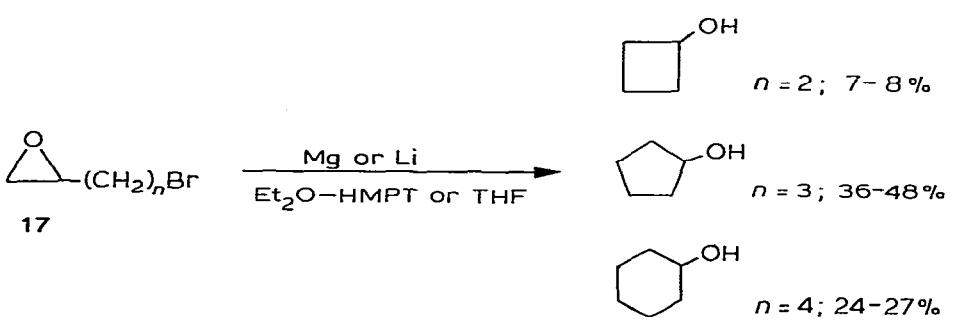
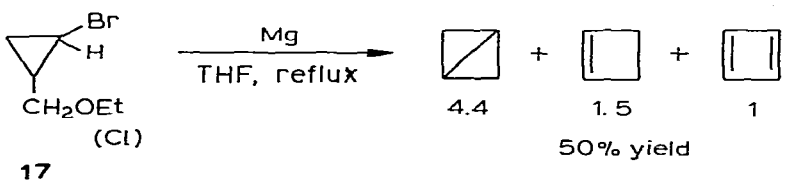
Refluxing epoxide 16 (n = 2–4) in THF or Et_2O–HMPT containing magnesium or lithium and CuI as activator for 60 hours gave cyclobutanol, cyclopentanol and cyclohexanol [28].



17

A new route to [1.1.0] bicyclobutane was described which is based on the reaction of 17 with magnesium in refluxing THF [29]. The reaction furnished a 50% yield of a mixture of [1.1.0] bicyclobutane, cyclobutene and cyclobutadiene.



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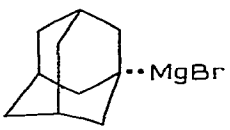
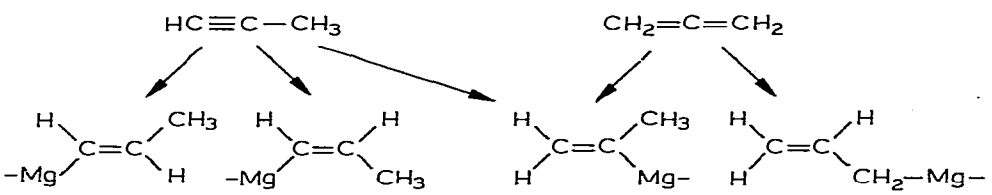
Theoretical consideration of the mechanism of decomposition of vicinal and geminal haloorganic compounds of lithium and other metals were published by Russian workers [30]. A concerted one-step mechanism for their decomposition (M = Li, Na, K, Mg, Ag, Hg, Cu, Al and B) via carbene and aryne formation, the driving force for which was intramolecular halogen-metal coordina-

tion, was discussed. Literature data were analyzed on the basis of this mechanism in terms of thermal effects on the decomposition, energy differences in the coordinating orbitals and the distance of the leaving atoms.

X-Rays photoelectron spectral analysis of the state of the surface formed during the reaction of 1-bromoadamantane with magnesium in the presence of CH_3CHBr_2 showed that the products, 1,1'diadamantane, magnesium and $MgBr_2$, are formed by disproportionation of the radical complex at the metal surface [31].



The structures of C_3H_5Mg intermediates formed in the reaction of propyne and allene with magnesium films were determined by converting them into propene-d_1 compounds, which were analyzed by micro-wave spectroscopy[6]. Propyne gave mainly the (E) prépenyl intermediate, while allene, although largely isomerized to propyne before reaction, gave both allyl and 2-propenyl intermediates, the first being slightly predominant. The formation of these intermediates was assumed to involve hydrometalation of propyne and allene by magnesium hydride.



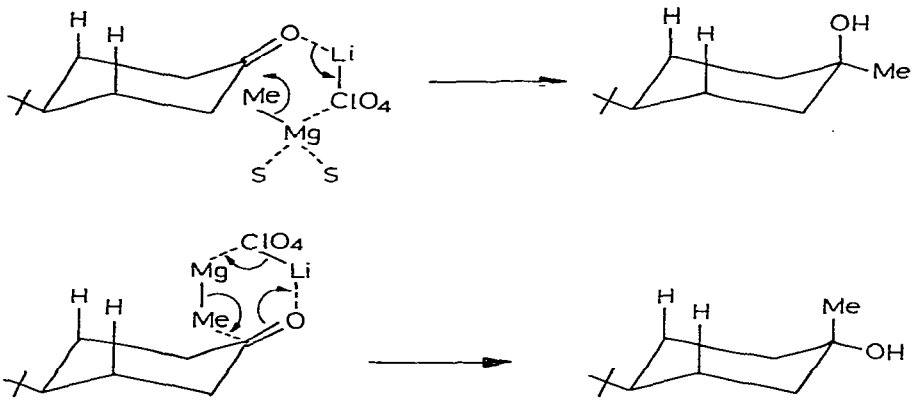
III. REACTION WITH >C = O BOND

A. Mechanism and stereochemistry of the addition to >C=O bonds

A 4- or 6- center single electron transfer process was found to occur at the rate-determining step in the reduction of benzophenone and azobenzene with Grignard reagents [32].

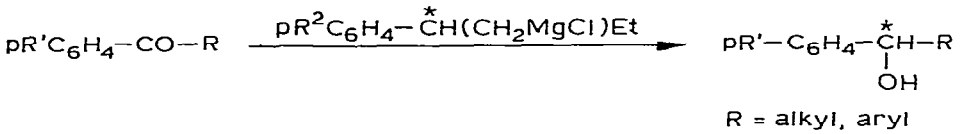
In addition to stereochemical effects, a major consequence of the presence of $LiClO_4$ in the reaction of ketones with Grignard reagents

was a dramatic increase in the rate of reaction, attributed to initial complexation of the ketone with $LiClO_4$ [33].

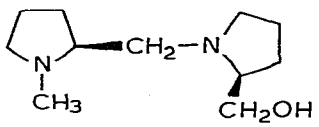


The substitution of benzene or toluene for ether in the Grignard reaction with hindered ketones led to a 75 % increase in yield [34]. An investigation of the interaction with mesityl ketones was performed using nitrogen-15 NMR spectroscopy [35].

Special effort was devoted to the field of stereoselective syntheses with organomagnesium reagents. The asymmetric reduction of diaryl ketones [36] and aryl alkyl ketones [37] was performed with chiral organomagnesium compounds.



The products were benhydrols with optical purities of ⩽37%. The absolute configuration and enantiomeric excess depend on electronic effects of substituents both in the Grignard reagent and the ketone. The addition of dialkylmagnesiums, R_2Mg, to aldehydes, R'CHO, in the presence of the chiral aminoalcohol 18 gave optically active alcohols, R'CHOH-R, the configuration and



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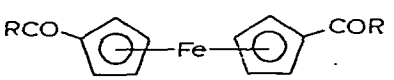
the optical yield, of which depended on the solvent, the reaction temperature and the nature of R [38]. The 1,2-addition of organomagnesiums to carbonyl compounds in chiral 1,4-bis(dimethylamino)-2,3-dimethoxybutane medium provided up to 70% enantioselectivity [39].

The stereoselectivity of the addition of organomagnesiums to 1,1'-diacylferrocenes 19 was studied. A preferred direction of the attack on the intermediate hydroxyketone (second attack) was suggested to be responsible for the selectivity [40].



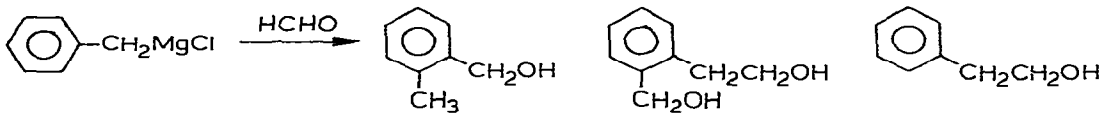
19

R = Me erythro diols
R = Et, Ph, Ph—CH_2 threo diols

The diastereoisomers of ortho- bis(α-hydroxyethyl) benzene were formed in 2:1 molar ratio in the reaction of MeMgCl with o-$C_6H_4(CHO)_2$ [41].

B. Reaction with aldehydes

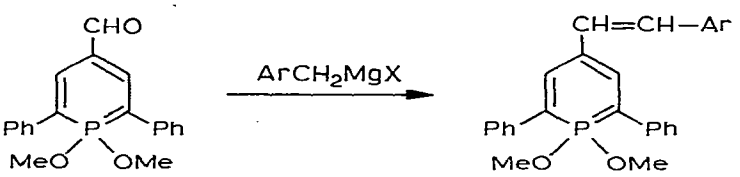
The reaction of benzylmagnesium chloride with formaldehyde [42] was found to give the alcohols 20 – 22.



20 21 22

The effect of concentration and nature of the formaldehyde used (monomer or polymeric) on the product distribution was discussed ; the intermediate leading to 21 was trapped by Me_3SiCl and characterized as o-$HOCH_2$-C_6H_4-CH_2SiMe_3.

The reaction of $CF_3(CF_2)_3SO_2CH_2MgI$ with formaldehyde was utilized in the synthesis of $CF_3(CF_2)_3SO_2CH{=}CH_2$ [43]. The unsymmetrical acetylenic synthon $(EtO)_2CH{-}C{\equiv}C{-}CHO$ allowed the sequential coupling of the aldehyde functions with different Grignard reagents [44]. The reaction of Grignard reagents with 3-formyltetrahydrofuran [45] and furfural [46] were described. The condensation of 1,1-dimethoxy-2,6-diphenyl-λ^5-phosphorin-4-carboxaldehyde 23 with a benzylic Grignard reagent gave 24 [47].



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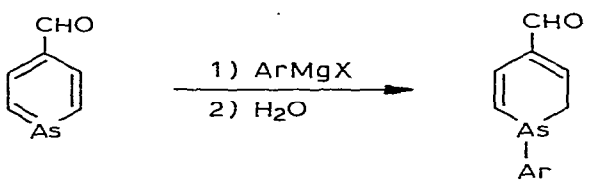
On the other hand, with arsabenzaldehyde the reaction of an aryl Grignard reagent resulted in the formation of dihydroarsenin carboxaldehyde 25 [48].



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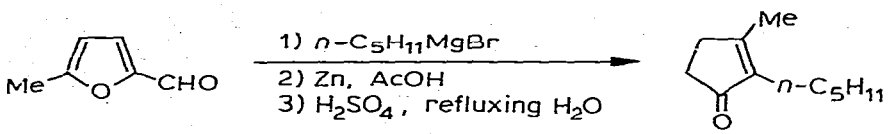
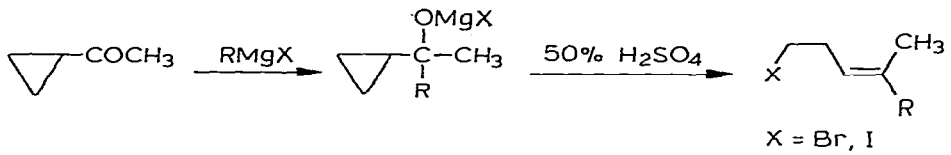
The condensation of n-pentylmagnesium bromide with 5-methyl-2-furfural was used as the first step in the synthesis of dihydrojasmone [49].



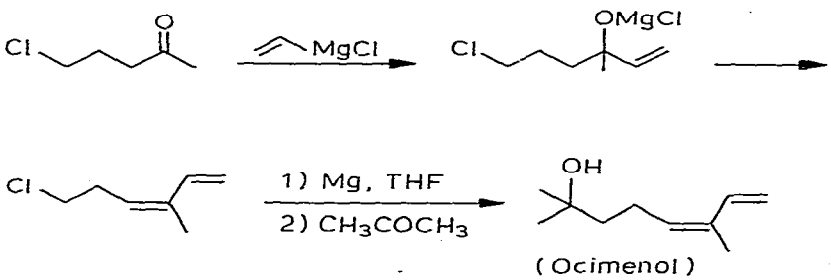
The coupling of methylmagnesium bromide with 1-naphthaldehyde was the first step of the synthesis of nor equilenium derivatives [50].

C. Reaction with ketones

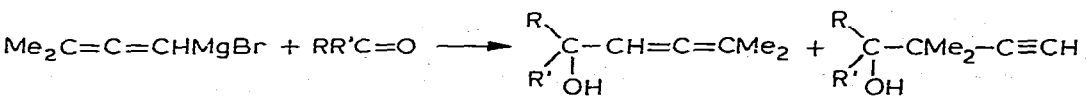
Methyl magnesium iodide was coupled with perhydrotriquinacen-2-one [51]. A modification of the method of JULIA for the preparation of homo-allylic bromides and iodides was described [52] which includes the hydrolysis of the halomagnesium alcoholates by 50% sulfuric acid.



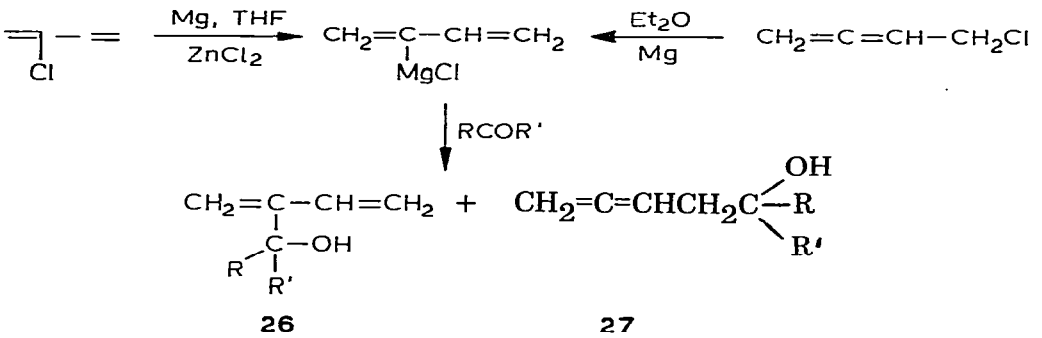
The synthesis of Ocimenol and related compounds was published where ethyl or vinyl Grignard reagents are coupled with 5-chloro-2-pentanone, and a dienic organomagnesium is coupled with acetone [53].



Various unsaturated Grignard reagents were coupled with ketones [11, 17, 18]. The reaction of γ,γ'-dialkyl-α-allenic organomagnesiums [54] with ketones gave a mixture of allenic and acetylenic alcohols.

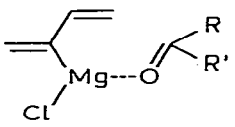


The Grignard reaction of R-CH=CR'-C≡C-CH_2Br with Me_2CO gave the alcohols R-CH=CR'-C=C=CH_2 [55]. Organomagnesiums compounds derived from
HO-CMe_2
allenic bromides were found to react readily with aliphatic and aromatic aldehydes and ketones to give in most cases a mixture of β-allenic and dienic alcohols [56]. 2-(1,3-Butadienyl)magnesium chloride afforded a mixture of the 1,3-dienyl alcohols 26 and the rearranged allenic alcohol 27 on reaction with carbonyl compounds and epoxides [57]. The formation of allenic alcohols is favored by lower basicity of solvent, by more covalent carbon-metal bonding and by increased steric hindrance in the ketone.

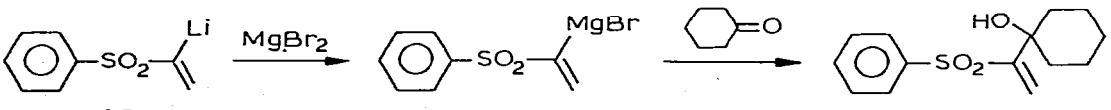


26 27

The regioselectivity of the reaction was consistent with a 6-menbered transition state 28.



α-Lithiovinyl sulfone 28 was converted to the Grignard analog by reaction with magnesium bromide. The new organometallic reagent gave better yields than its lithioprecursor in the coupling reaction with enolizable carbonyl substrates such as cyclohexanone [58].



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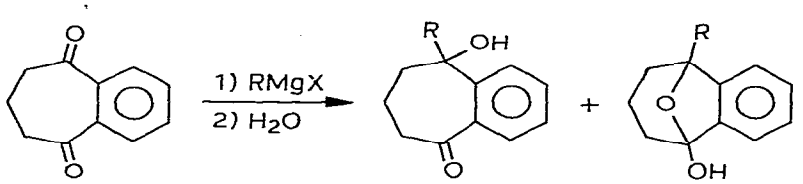
Grignard reagents were condensed with several α-ketoamides for the preparation of unsymmetrically disubstituted glycolic acids [59]. The Grignard alkylation of Isatin was performed [60].

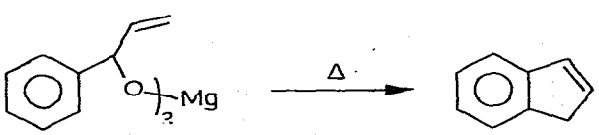
Branched chain sugars were prepared by reaction of hexafuranosulose with organomagnesium reagents [61]. The reaction of various Grignard reagents with 4-chromone [62], naphthacyclobutene-1,2-dione [65], various 2,2-disubstituted derivatives of cyclopentanone [63], 5-methoxy-3-methylindanone [66] 2-phenyl-3*H*-indol-3-one [67], 3-oxo-1-pyrroline-1 oxides, 4-quinolinones [69] were described.

The Grignard reaction of benzocycloheptanedione 29 gave tautomeric benzocycloheptenols [64].



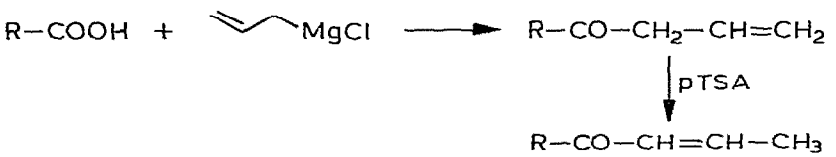
The condensation of vinylmagnesium chloride with 2-chlorocyclododecanone, followed by heating and hydrogenation of the resulting product, gave cyclohexadecanone via ring enlargement [70]. The rearrangement of α,α-dichloroalkyl aryl ketones [71, 72] and 1-aryl-2,2-dichloro-1-alkanols with methylmagnesium iodide was studied. $PhCO-CCl_2R$ reacts with MeMgI to give $Ph-CRMe-CMe_2OH$ via a pseudopinacol-type rearrangement.

A novel isomerization of magnesium alcoholates occured during the course of the synthesis of the 6-methylenebicyclo [3.1.0] hex-2-ene system [73]. Magnesium alkoxide 30 was found to undergo a cationic cyclization by thermolysis. Thus solid state thermolysis of Mg salts of 1-substituted 1-phenylallylalcohol result in efficient indene formation [74].

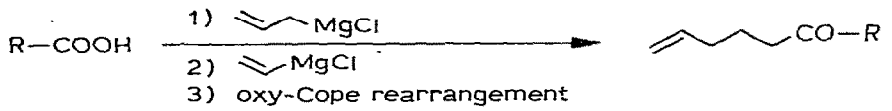


D. Reaction with acids and esters

Various allyl ketones were prepared from carboxylic acids and CH_2=CH-CH_2MgCl [75],



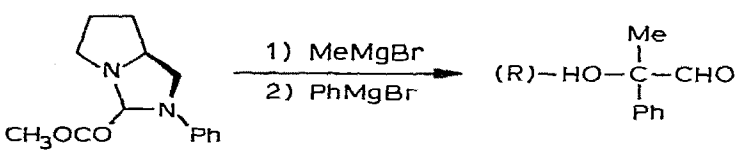
while the reaction of allylmagnesium chloride with acids, followed by vinylation with vinylmagnesium chloride and oxy-cope rearrangement, afforded δ,ε-ethylenic ketones [76].



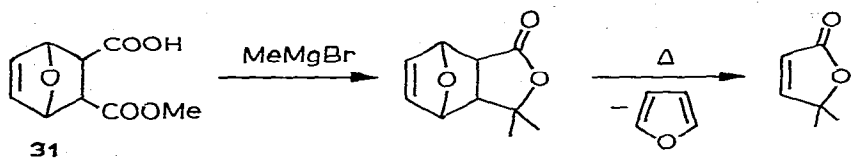
In the reaction of salicylic acids with Grignard reagents, it was found that the addition of nickel increased the yield of keto products [77], the stabilization of which in the form of ketyl radicals was verified by an E.S.R. study [78].

The reaction of the Grignard reagent derived from $ROCH_2C{\equiv}C$-Br with esters, R'COOEt, gave $(ROCH_2C{\equiv}C)_2CR'OH$ [79].

A convenient method for the preparation of optically active α-hydroxyaldehydes with desired configurations by reaction with the methoxy carbonyl aminal 30 was described [80].

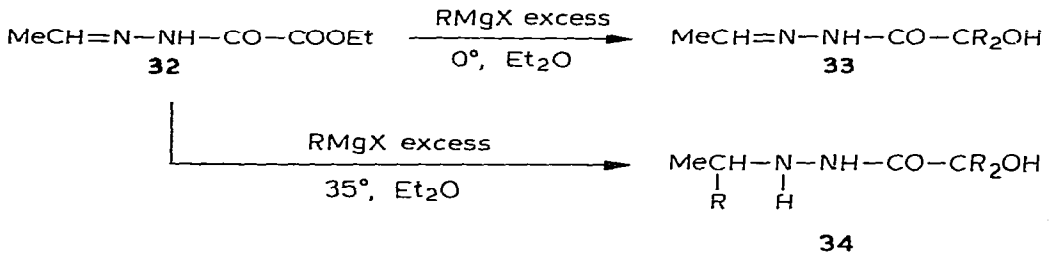


The synthesis of dialkylfuranone was achieved by addition of Grignard reagents to the monoester of the diacid 31 [81].



31

The reaction of organomagnesium reagents with 32 [82] was found to give 33 at 0° and 34 in refluxing ether.

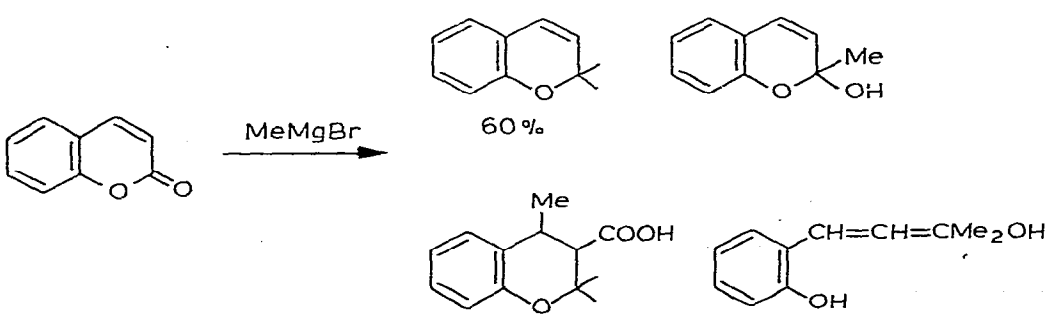


32 33 34

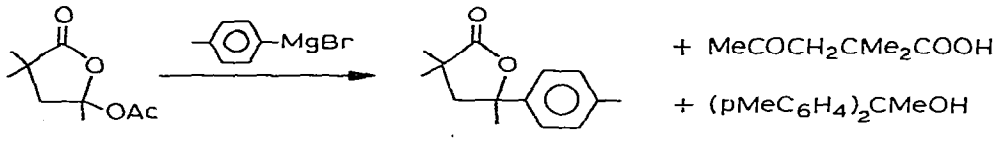
The reaction of 3-quinolylmagnesium bromide with dialkyl oxalates was published by Russian workers [83].

E. Reaction with lactones and lactams

The Grignard reaction of coumarin with MeMgBr gave a 60% yield of 2,2-dimethyl-3-chromene [85], along with 9 other compounds :

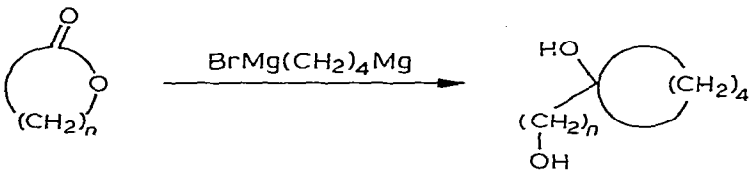


Me-C6H4-MgBr reacted with the lactone 35 to yield lactone 36 [86] :

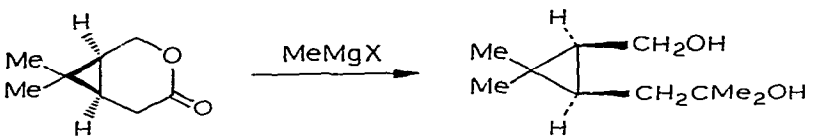


35 36

Ring opening of lactones by di(bromomagnesio)alkanes was found to afford diols [86].



Methyl magnesium halides were utilized in the preparation of cyclopropanic diols [87] :

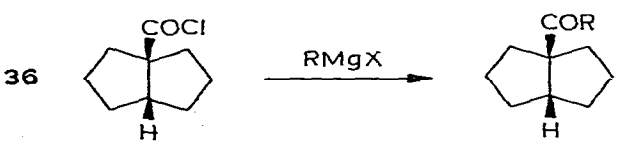


Propargyl Grignard reagent, on reaction with butyrolactone, was shown to give 2,2-dipropargyltetrahydrofuran in 26% yield [88].

The reactions of benzylmagnesium chloride with differently substituted 2-azetidones [89], and also of aryl magnesium bromides and benzylmagnesium bromides on cyano(aryl)methylene phthalides [90] were studied.

F. Reaction with acyl chlorides and fluorides

The reactions of Grignard reagents and organocadmium compounds with 36 were studied with the object of synthesizing bridge head carbonyl derivatives [91].

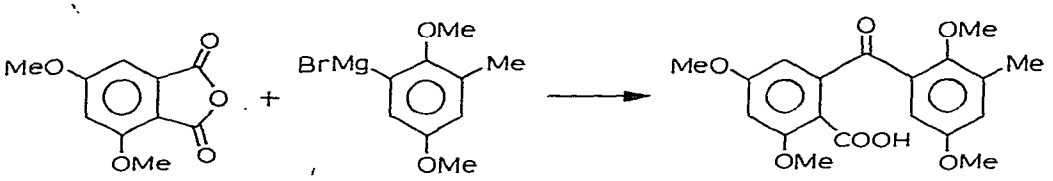


2-Methyl-1-naphthoic acid chloride was treated with 2-methyl-1-naphthylmagnesium bromides [92]. Benzylmagnesium chloride reacted with methyl chloroformate to yield $PhCH_2COOMe$ and $o\text{-}MeC_6H_4CO_2Me$ 37, together with a trace of $o\text{-}MeOCOC_6H_4\text{-}CH_2\text{-}COOMe$ [93]. The influence of various parameters, among them polarity of solvent, on the formation of 37 was discussed.

The reaction of perfluoro alkylmagnesium reagents with aliphatic perfluoro acid fluorides gave low yields of the respective perfluoroketones as well as undesired side products. The coupling of the corresponding perfluorinated copper compounds gave perfluoro ketone yields [94].

G. Reaction with anhydride

1,2-Naphthalic anhydride reacted with the Grignard reagent derived from 5-bromo-1,2-dimethoxy naphthalene to give a ketoacid [95]. The reaction of 3,5-dimethoxy phthallic anhydride with 3-methyl-2,4-dimethoxyphenylmagnesium bromide furnished the adduct 38 as the first step of the preparation of catenarin and erythro-glaucin [96].



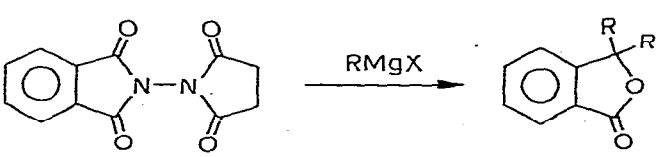
38

H. Reaction with various carbonyl-containing compounds

The reaction of trimethylsilylmethylmagnesium chloride on diketene in the presence of $NiCl_2$ was applied to the preparation of

$Me_3Si\text{-}CH_2\text{-}C(=CH_2)\text{-}CH_2\text{-}COOH$ [97]

Reactions of Grignard reagents with mixed diimides gave phthalides [98].



A new route to tetraphenylpyrrole derivatives included reaction between 2-benzylidene-4-phenyl-5(2H)-oxazolone and phenylmagnesium bromide [99].

The carbonation by CO_2 of Grignard and organolithium reagents was achieved in good yield in the presence of manganese(II) chloride [100]. o-Trifluoromethyl benzoic acid was synthetized by carbonation of o-trifluoromethylphenylmagnesium chloride [101].

IV. REACTION WITH >C=S BONDS

The synthesis of dithiocarboxylates, $R-CS_2Me$ was accomplished by coupling RMgX with CS_2, followed by treatment of the RCS_2MgX with MeI [102], while a convenient method for the preparation of methyl trithioperesters included addition of RMgCl in THF to CS_2 and treatment of the resulting magnesium dithiocarboxylate with methyl methanethiosulfonate [103].

$$RMgX + CS_2 \longrightarrow R-CS_2MgX \xrightarrow{MeI} R-CS_2Me \quad [102]$$

$$R-CS_2MgX \xrightarrow{MeSSO_2Me} RCS_2SMe \quad [103]$$

The reaction of Grignard reagents with triphenyl-dithiocyanatophosphorane proved to be a versatile route to N-unsubstituted thioamides [104] (via hydrolysis of the intermediate 39 which can be trapped by methylation as 40).

$$Ph_3P(SCN)_2 + RMgX \longrightarrow Ph_3P{=}N-\underset{\displaystyle R}{\overset{\displaystyle |}{C}}{=}S \xrightarrow{H_2O} R-\overset{\displaystyle S}{\overset{\displaystyle \|}{C}}-NH_2$$

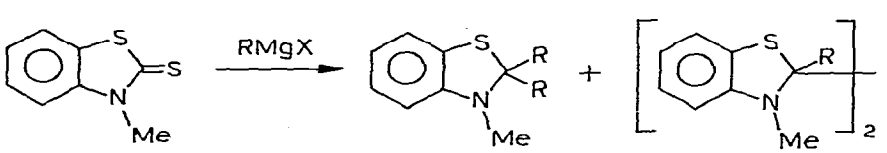
39

$$\downarrow MeI$$

$$Ph_3\overset{+}{P}-N=\underset{\displaystyle SMe}{\overset{\displaystyle R}{C}}\ I^-$$

40

The reaction of aryl thiobenzamides, $ArC(=S)NH_2$, with arylmagnesium bromides gave 1,2-addition products, i.e., imines and thiones [105]. The condensation of Grignard reagents with 41 was studied [106].

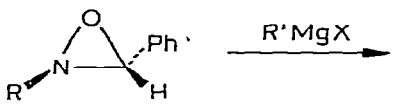


41 **42**

The formation of 42 as a byproduct was shown to be due to the presence of transition metals as impurities in the magnesium used.

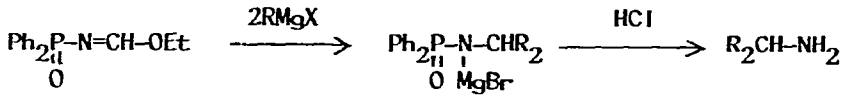
V. ADDITION OF ORGANOMAGNESIUM COMPOUNDS TO A CARBON-NITROGEN BOND

The reaction of Grignard reagents, R'MgX, with 43 led to coupling and hydroxylation of the R' group, depending upon R substituent [107] :



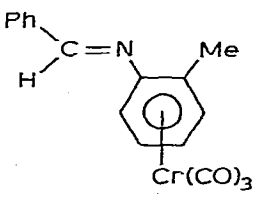
A. Réaction with >C = N-Bonds

The Grignard reaction of 44 with RMgX gave 79-86 % yields of 45, the protolysis of which by HCl in THF at room temperature furnished primary amines [108].

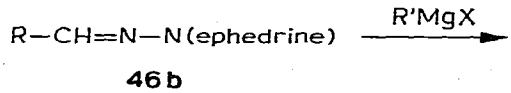


44 45

Asymmetric induction in the addition of Grignard to >C=N-bonds was studied. The addition of a Grignard reagent to the benchrotene derivatives of diaryl imines 46a proceeded with a high degree of asymmetric induction [109]. Chiral hydrazones of aldehydes 46b added organomagnesium compounds in almost 100% diastereoisomeric excess [110].

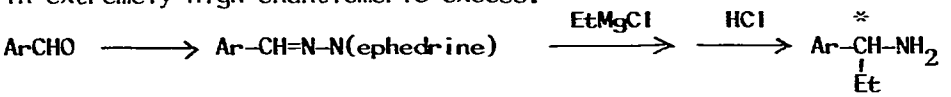


46a [109]



46b [110]

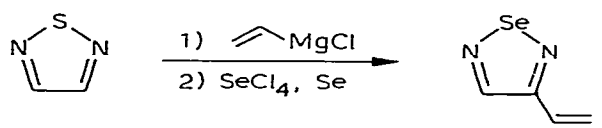
This last reaction was applied to the synthesis of (R)-α-phenylalkylamines in extremely high enantiomeric excess.



Chemical yield	89%
Optical purity	96%

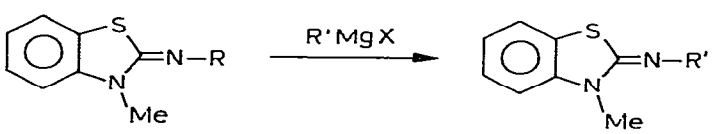
Other types of Grignard addition to >C=N- bonds were reported : N(o-methoxy-benzylidene) aniline [111], 3-anilino-4-arylhydrazono-2-pyrazolin-5-ones [112], purines [113].

Thiadiazole 47 on reaction with vinylmagnesium chloride, followed by treatment with selenium chloride gave the vinyl thiadiazole 48 [114].



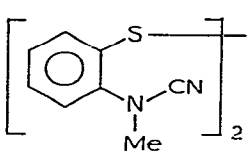
47 48

The addition of the Ivanoff reagent to azirine double bonds was described [115]. The addition of Grignard reagents to 49 gave 50 as the major-product [116].



49 50

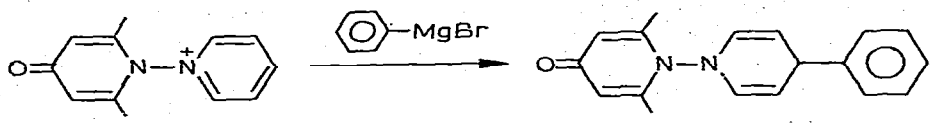
R = pMePhSO3-
Me3SiO-
MeO-



51

Iminium salts were involved in the synthesis of an antiviral nucleoside [117] and a tetrahydro iso quinoline [118].

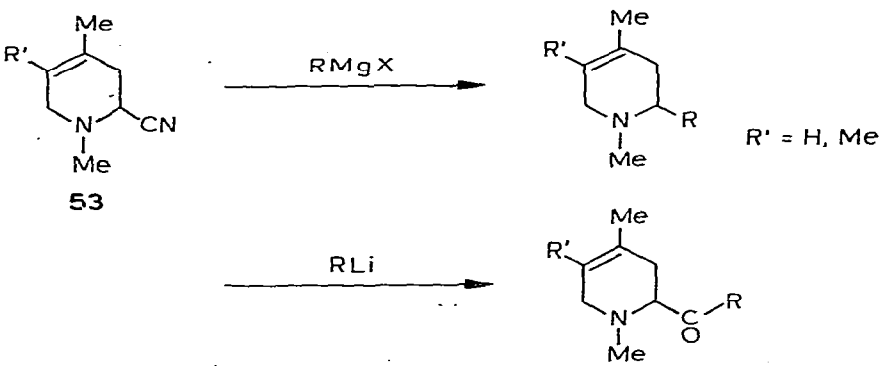
The 1,4-addition of Grignard reagents to pyridinium salts 52 was found to allow the synthesis of 4-substituted pyridines [119, 120].



52

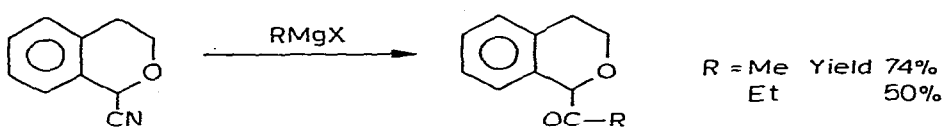
B. Reaction with Nitriles

Thenoyl quinolizidine was prepared by addition of thienyl magnesium halide to a 3-cyanoquinolizidine [121]. 2-Cyanotetrahydropyridine 53 reacted with RMgX with substitution of the Cyanogroup, but addition to the cyano group was observed with organolithium reagents [122].

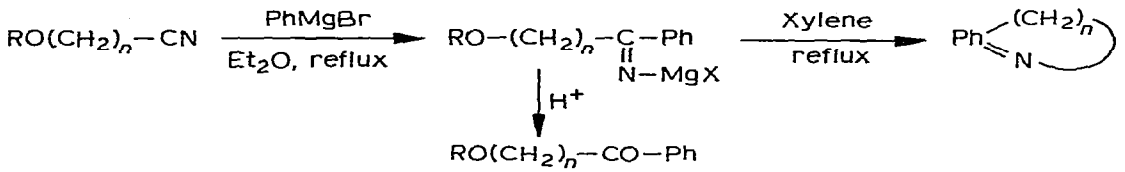


53

54 was shown to undergo addition to the -C≡N bond [123].



The reaction of organometallic reagents, Ph-M (M = Li, MgX), and nitriles, $RO(CH_2)_nCN$, was studied (R = alkyl, Ph ; n = 3,5) [124]. The products formed depend on the reaction temperature. In refluxing ether, only the monoaddition ketone $RO(CH_2)_n$-CO-Ph was obtained in good yields. In refluxing xylene, the intermediate ketoimidate underwent intramolecular cyclization.



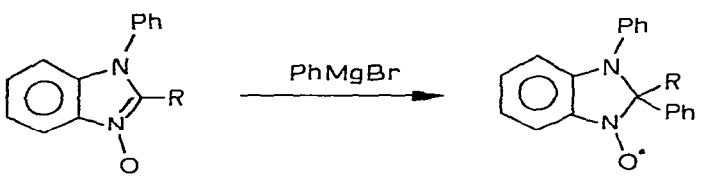
Treatment of cyanogen with 2 equivalents of Grignard reagents gave a mixture of glycinonitrile 55, ketone and tertiary alcohol [125].

$$R\text{-}MgX + CN\text{-}CN \longrightarrow \underset{55}{R_2C(CN)NH_2} + R\text{-}CO\text{-}R + R_3COH$$

The glycinonitrile 55 was shown to be formed via two successive additions to one of the cyano groups of cyanogen and was stable only when R = Ph. When R = alkyl, the intermediate 55 underwent either elimination of cyanide to give ketones, R_2CO, or substitution of the cyano group to give R_3COH.

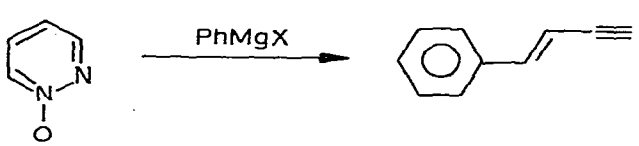
C. Miscellaneous Reactions

The reactivity of benzimidazole N-oxides 56 with PhMgBr was studied. The reaction was found to give stable nitroxide radicals 57 [126].



56 57

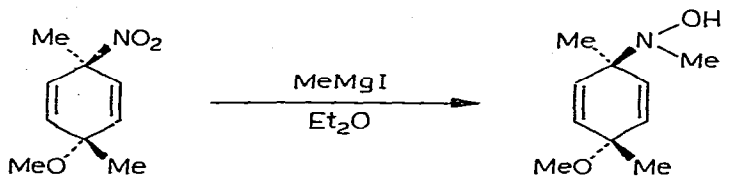
Terminal enynes were synthetized by Grignard addition to pyridazine N-oxide 58 [127].



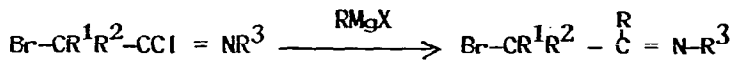
58

The formation of radicals was suggested to occur during the reaction of nitrosodurene with Grignard reagents [128]. The ipso methoxynitro adducts of p.xylene 59 yielded 60 [129]. The selectivity of attack in

nucleophilic alkylation of nitro arenes was reported [130].



The reaction of Grignard reagents with α-chloroaldimines 61 led to the corresponding bromoketimines 62 [131] via chlorine substitution.



61 62

VI. ADDITION TO CARBON-CARBON MULTIPLE BONDS

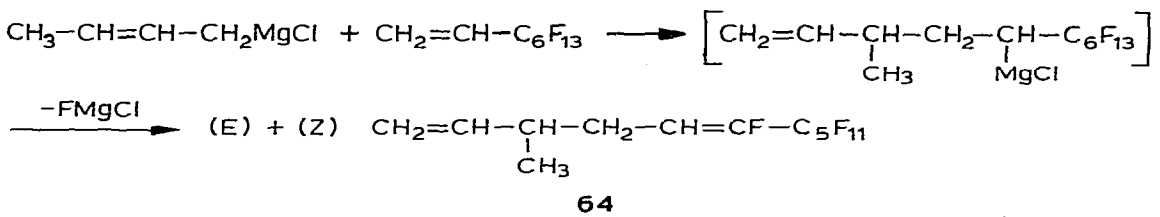
The carbomagnesiation of 1,1-diphenylalkenols by various Grignard reagents (allyl ; benzyl ; tert-butylmagnesium bromides) in diethyl ether and diallylmagnesium in benzene was studied [132]. From the observation of structural features, effects of solvents and catalysis by nickel complexes, a mechanism for the uncatalyzed carbomagnesiation was proposed, which included as an essential step the rearrangement of an alkenoxy(alkyl)magnesium intermediate 63 :

63

The stereochemistry of carbomagnesiation of 2-cyclopentenol, 3-cyclopentenol and various unsaturated cycloalkanols with allylmagnesium bromide indicated that the directing effect of the hydroxyl group arose from the formation and intramolecular rearrangement of an allylmagnesium alkoxide of type 63 (R = ∿). The proximity of the allyl-magnesium bond to the ⟩C = C⟨ function in 63 facilitated electrophilic attack by magnesium with syn addition [133].

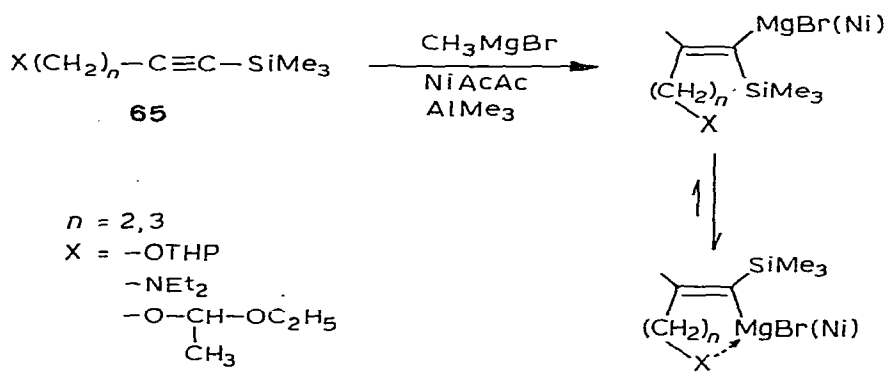
The reaction of phenyl magnesium bromide with 1,3-butadiene in the presence of nickel(0) complexes was found to provide a new route to phenyl polyene hydrocarbons [134]. The addition of Grignard reagents to chro-

mene was investigated [134]. Perfluoroalkyl ethylenes were found to undergo addition of crotyl magnesium chloride to give 1,5 dienes 64 via addition-elimination [136].

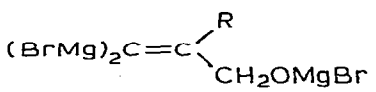


64

The nickel-catalyzed carbometallation of functionalized silyl-alkynes 65 by Grignard reagents led to the formation of stabilized magnesio vinyl silanes [15]. The reaction was applied to the synthesis of geraniol and farnesol.



α-Acetylenic [11,13] and α-allenic [12,13] alcohols were shown to undergo regio- and stereospecific addition of Grignard reagents in the presence of cuprous halides. The same reaction occurred with metallated propargylic alcohols and gave the poly magnesium compounds of type 7 [14] (cf. II B).



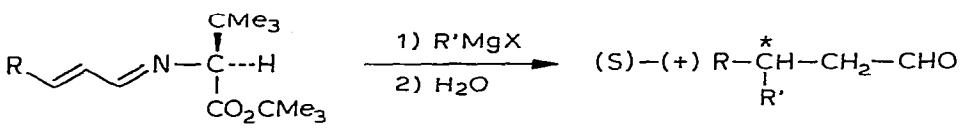
7

The addition of Grignard reagents to cyclopropenes followed by carbonation gave cyclopropane carboxylic acids [137]. In the presence of benzyne, allylic Grignard reagents were found to undergo three competitive reactions : nucleophilic addition and $(\pi^2 + \pi^2)$ and $(\pi^4 + \pi^2)$ cycloadditions while with cyclohexyne, only nucleophilic addition was observed [138]. The addition of Grignard reagents on various activated olefines was described : diaroyl-

ethylenes [139], furochalcones [140], 3-substituted coumarins [141], aroylamido ethylenes [142], irigenin trimethyl ether [143], 5-benzylidene-2-thiazolin-4 ones [144]. The 1,4-addition to pyridinium salts afforded 4-substituted pyridines [118, 119] (cf. IV.A). It was shown that single electron-transfer was not involved in the reaction of organomagnesium compounds with chiral α,β-ethylenic esters [145]. The reaction of 1-iodo-1-octene-3 one with alkylmagnesium bromides [146]gave a mixture of products resulting from competitive initial 1,2 and 1,4 additions. Methylene-benzothiochromanone was shown to undergo 1,4-addition [147].

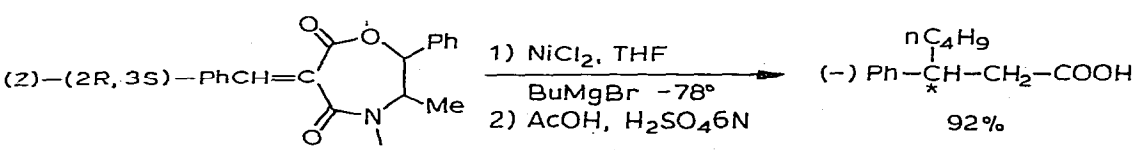
Inversion of stereoselectivity in the conjugate addition to (-)-menthyl crotonate occurred in the presence of catalytic amounts of Cu^{+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Mn^{2+} or Ni^{2+} [148]. The mechanism of the catalytic activity of these cations was suggested to involve complexation by the transition metal cation at the least hindered face of the intermediate cyclic complex between the ester and the Grignard reagent, followed by further Grignard attack on this new shielded complex at the other side.

The stereo selective 1,4-addition of Grignard reagents to optically active α,β-unsaturated aldimines 66 proved to be a highly efficient asymmetric route to optically active β-substituted aldehydes with up to 91 - 98% enantiomeric excess [149].



66

The asymmetric synthesis of 3-alkylsuccinaldehydic acid methyl esters was performed by addition of Grignard reagents to HCO-CH=CH-COOMe, the aldehyde function being transformed into an animal group from (S)-2-anilinomethyl-pyrolidine [150], while optically active propionic acid derivatives were obtained from the methylene cyclic malonic amido ester 67, in high enantiomeric excess [151].



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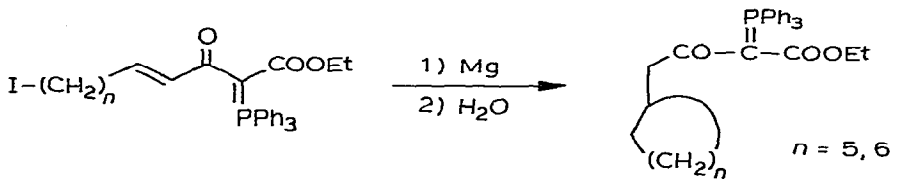
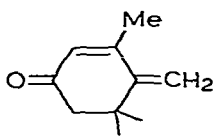
The action of magnesium on products 68 led to cyclic compounds via intramolecular Michael addition of an intermediate Grignard reagent [152].



Competitive 1,2 1,4 and 1,6 additions were observed with the ketone 69 in THF [153]. The presence of CuBr enhanced the tendancy to give 1,6-addition



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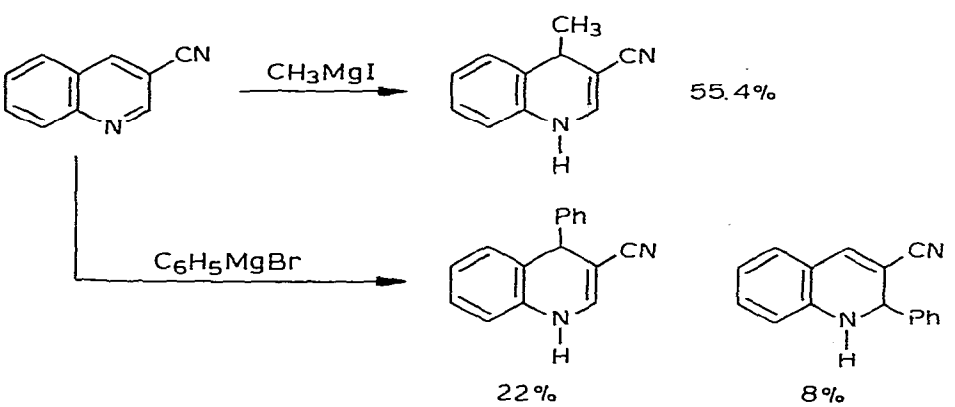
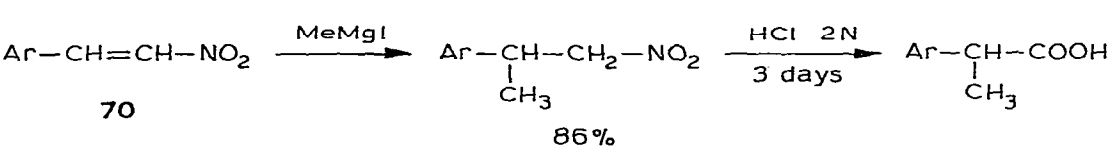
Isophorone was subjected to addition of an α-silyl-Grignard reagent [154]. 1,4-Addition of methylmagnesium iodide and phenylmagnesium bromide to 3-quinoline carbonitrile was observed [155].

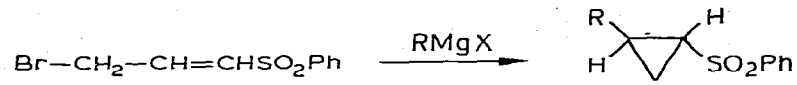


Phenylacetic acid derivatives were synthetized [156,157] from β-nitro-styrenes 70.



Cyclopropanes were obtained from addition of Grignard reagents to 3-substituted 1-alkenylsulfones 71 [158].

References p. 39



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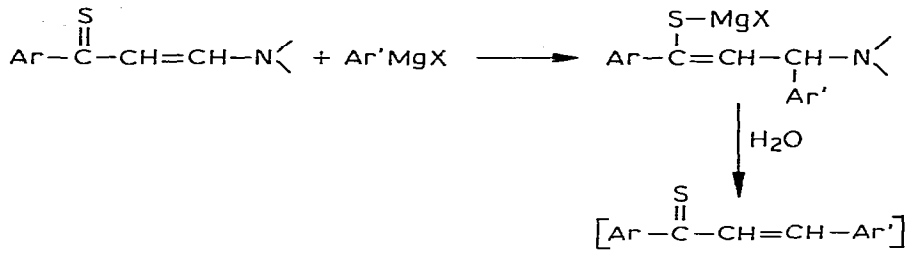
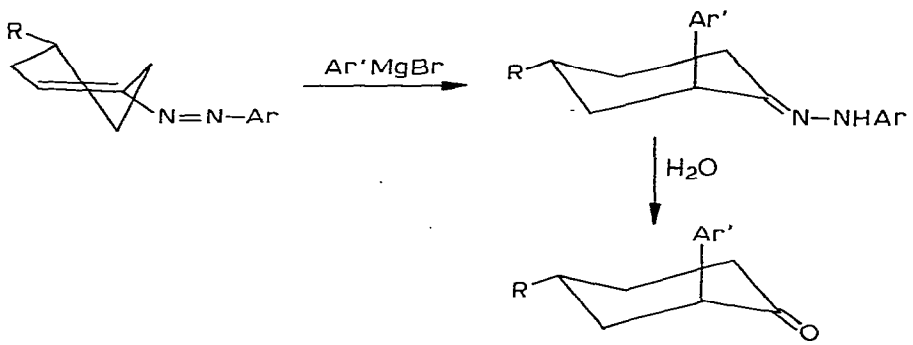
The addition of ArMgX to β-aminothiochalcones [159] led to unstable thiochalcones, which could be trapped with acrylic esters



Aryl azocyclohexenes 72 added arylmagnesium bromides to give, after oxydative hydrolysis, 80–5 % yields of trans-cyclohexanones [160].

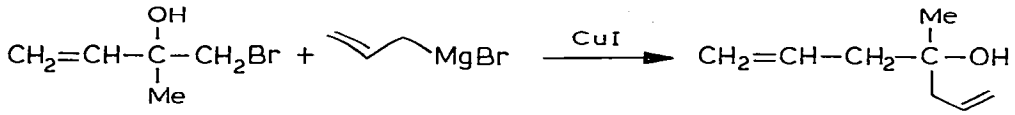


VII. DISPLACEMENT REACTIONS BY ORGANOMAGNESIUM COMPOUNDS

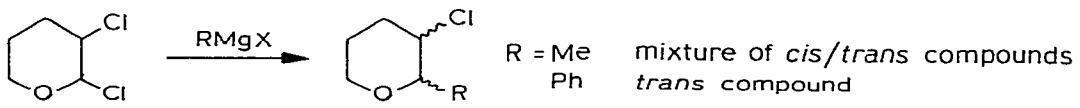
A. Coupling Reactions with Organic Halides

Benzyl bromides reacted with methylmagnesium halides in the presence of alkylpalladium(II) complexes to give ethylbenzenes with inversion of configuration through reductive elimination of a palladium(IV) intermediate [161]. A general method for preparing α,α'-branched acetylenes was proposed, including the reaction of propargylic halides with Grignard reagents [162].

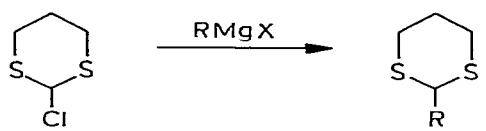
The reaction of tetrahaloneopentanes with Grignard reagents was shown to produce CH_2=CMeEt as the main product [163]. A highly selective vinyl rearrangement was found in the reaction of isoprene bromohydrin [164] with allylic magnesium compounds in the presence of CuI.



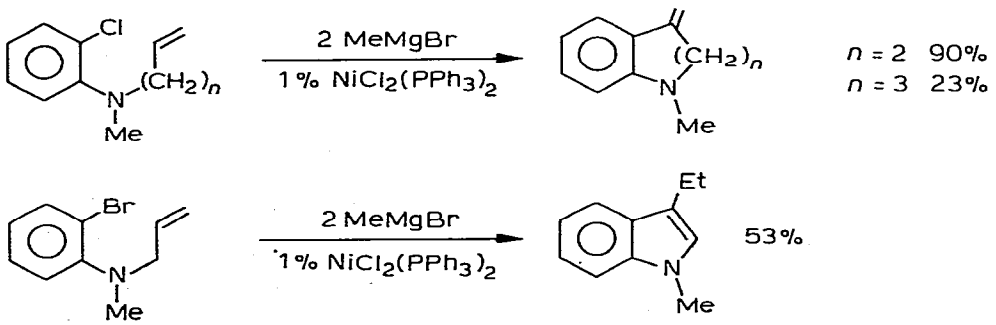
Grignard reaction of cis/trans 2,3-dichlorotetrahedrypyran gave a mixture of cis/trans 2-methyl-3-chlorotetrahydropyran with methyl-magnesium bromide and only the trans compound with phenylmagnesium bromide [165].



A synthesis of dithianes was effected by coupling primary alkyl, aryl, vinyl and secondary alkyl Grignard reagents with 2-chloro 1,3-dithiane [166].



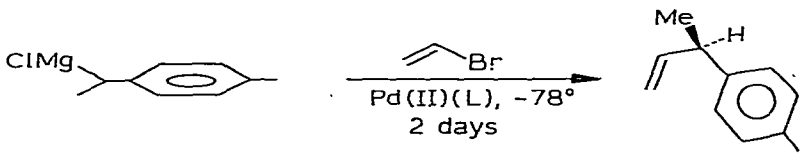
ω-Bromo esters were alkylated by Grignard reagents in the presence of a catalytic amount of Li_2CuCl_4 (37 - 79 % yield), while ω-bromo aldehydes were found to undergo only hydroxyalkylation [167]. Aromatic and vinylic halides were coupled with RMgX in the presence of various transition metal complexes as catalysors [168-171]. A nickel(II) chloride complex was used in a cyclization reaction leading to indole, quinoline and benzazepine [169].

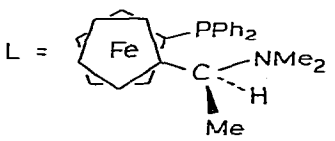


Sec-butylmagnesium halides, on coupling with phenylhalides in the presence of a chiral complex of nickel chloride, allowed the synthesis of optically active 2-phenylbutane [168]. Optical purity and configuration of the products depended upon the nature of the halogens displaced and on the organic moieties :

$$ArX + \text{sec Bu—MgX}' \xrightarrow[\text{phosphino propane}]{NiCl_2[(+)\text{-(R)-1,2 bis diphenyl-}} Ar\overset{*}{C}H(CH_3)-C_2H_5$$

The same types of coupling with aromatic and vinylic halides were effected in the presence of palladium(II) complexes [170,171]. An optically active ligand of palladium(II) [(S)-(R) aminoalkyl ferrocenyl] diphenyl phosphine 72 was used in the synthesis of (R)-(-)-α-curcumene with 66% optical yield and 34% overall yield in five steps, the key one being the coupling of a benzylic Grignard reagent with vinyl bromide [171].





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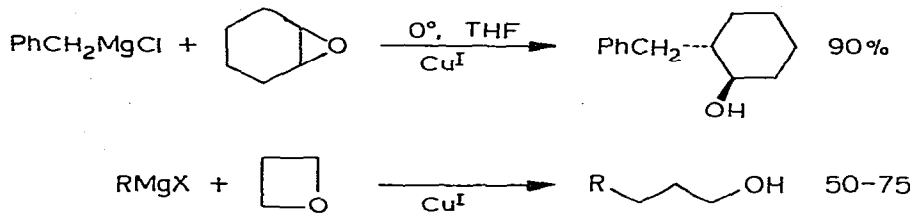
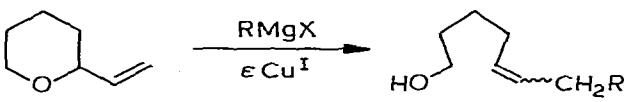
Similarly, the condensation of Grignard reagents with 8-bromo-purines and 8-bromoadenosine 3',5'-cyclic monophosphates was performed in the presence of palladium and nickel complexes for the modification of position 8 of purine nucleosides and adenosine 3',5' cyclic monophosphates [172, 173].

B. Displacement Reaction at C-O, C-S and C-S Bonds

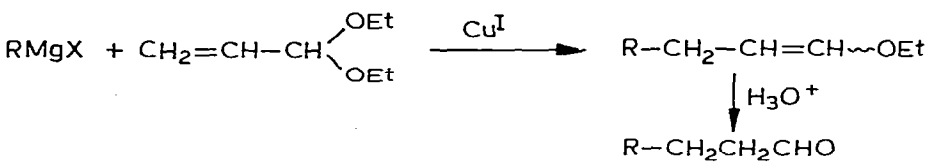
The reaction between 1,2-epoxycyclohexane and magnesium derivative of 3-bromo-1-propyne was investigated [174]. The ring chavage of oxetanes and epoxides was shown to be catalyzed by copper(I) salts [175].

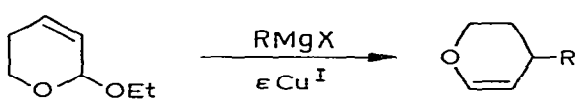


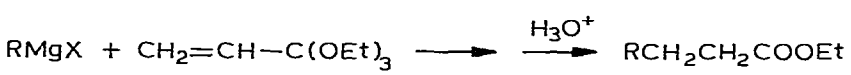
Alkenes have been prepared by Cu(I)-catalyzed substitution of allylic ethers by Grignard reagents [176]. Only primary aliphatic Grignard reagents gave good yields. Allylic cyclic ethers reacted if the furan or pyran ring was saturated.



Substitutions of α-ethylenic ketals and α-ethylenic orthoesters [177] were performed in the same way





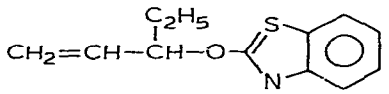


The mechanism of the substitution of allylic ethers by Grignard reagents was investigated with substituted cyclohexenols [178]. It was found that the leaving alkoxy group must be quasi-orthogonal to the plane of the double bond.

Reduction was also encountered during such reactions, especially with phenyl-substituted allyl ethers and acetates [179]. It seemed that the

relative amount of reduction increased with electron delocalization in the postulated copper(III) bound allyl ligand and also was dependent on the nature of the leaving group. The alkylation of allylic tosylates [180] and ethers [181] was used in the synthesis of pheromones.

Other substrates can replace the ether function : benzothiazole 73 [182], 2-pyridyl ether 74 [183], 2-pyridinium salts 75 [184].



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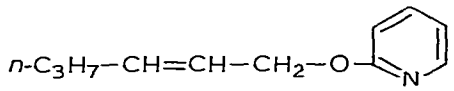

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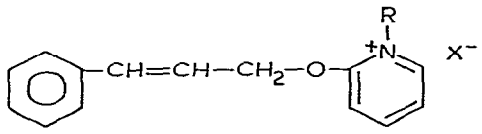

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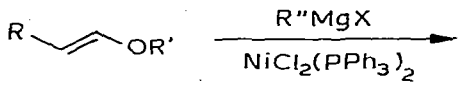
The reaction of Grignard reagents with unsaturated 2-oxinanes was investigated [185]; stereospecific 1,4 substitution occured with an α-unsaturated epoxide and was utilized in the synthesis of 11 β-substituted 19-norsteroids [186]. Allylic sulfones also underwent allylic substitution by Grignard reagents in the presence of $Cu[CH(COOEt)_2]$; the regio and the stereospecificity of this reaction were studied [187]. Treating organomagnesium compounds with α,β-acetylenic sulfones gave higher acetylenes and sulfinate salts [188].

$$Ar\text{-}SO_2\text{-}C{\equiv}C\text{-}R + R'MgX \longrightarrow ArSO_2MgX + R'\text{-}C{\equiv}C\text{-}R$$

In the presence of copper salts, propargylic ethers [189,192], acetates [190], tosylates [191] and propargylic ammonium salts [192] reacted with Grignard reagents to give allenes. Propargylic optically active ethers and ammonium salts served in the preparation of chiral allenes [192] which, however, were shown to be racemized rapidly (3 hours at -30°) by MeMgI/CuI (4/1) in Et_2O-THF [193].

Enol ethers [194], enol sulfides, benzenethiol derivatives [195, 196], and heterocyclic sulfides [197] were found to undergo oxygen or sulfur displacement by Grignard reagents in the presence of nickel chloride-phosphine complexes.



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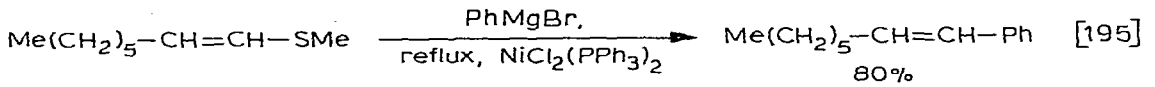

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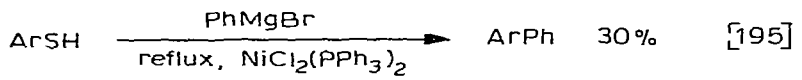

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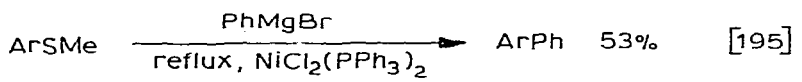

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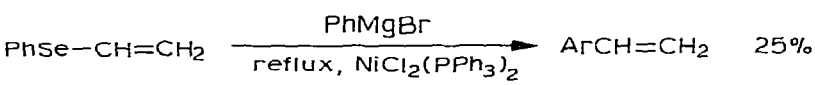

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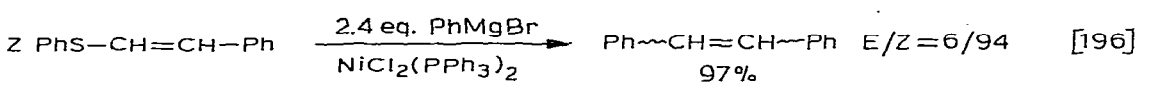

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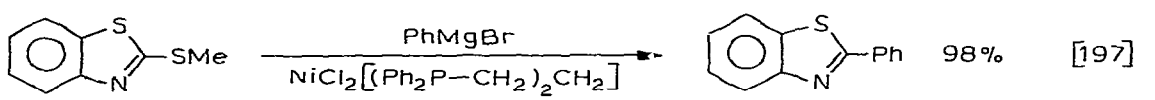
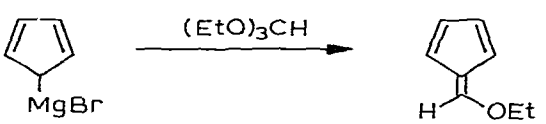


[197]

Cyclopentadienylmagnesium bromide reacted with triethyl orthoformate, to give 6-ethoxy fulvene in 50% yield [198,199].



The reaction of non-solvated diphenylmagnesium with alkylperoxides was investigated [200].

Cyclopropane quinolines 76, on treatment with organomagnesium reagents, led to the formation of 77 [201] with substitution of a methoxy group, and the C-alkylation in Grignard reaction of α-phenyl dihydro cinnamonitriles was reinvestigated [202].

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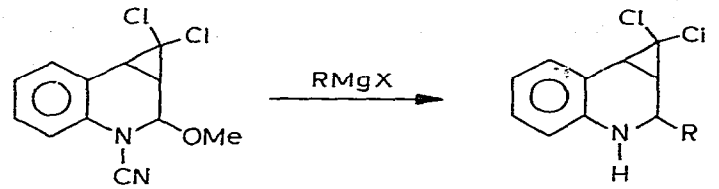

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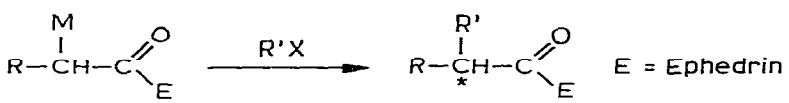
VIII. FORMATION AND REACTIVITY OF MAGNESIUM ENOLATES

The second order reaction between a Grignard reagent, RMgBr, and an alkyl mesityl ketone, 2,4,6-$Me_3C_6H_2CO$-R', in Et_2O was followed measuring the rate of alkane evolution [203]. Rapid, reversible formation of a complex between the ketone and RMgBr was postulated, with the rate-determining step being the removal of an hydrogen atom from the α-carbon, in a 6 membered cyclic transition state, to form the alkane and the enolate.

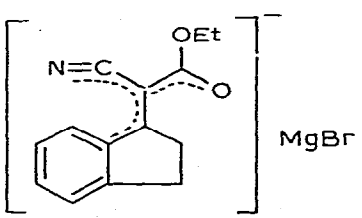
The reactions of phenylacetic amides with benzaldehyde in the IVANOFF and REFORMATSKY conditions were investigated [204].

The asymmetric alkylation of the carbanions (M = Li, MgX) derived from amides of l or d-ephedrine was published [205]. A study of the reaction characteristics indicated that the nature of the counter ion (Li or Mg) is the critical factor in the asymmetric synthesis



In this way (S)-(+)-4 methyl-3-heptanone, an alarm pheromone of "Atta Texana", was synthezed in 81% enantiomeric excess.

Ethyl-2-(1-indanylidene) cyanoacetate was treated with phenylmagnesium bromide to give the ambidant anion 78 [206] which gave α and β alkylations and hydroxyalkylations in the presence of alkylating reagents and aldehydes, respectively.



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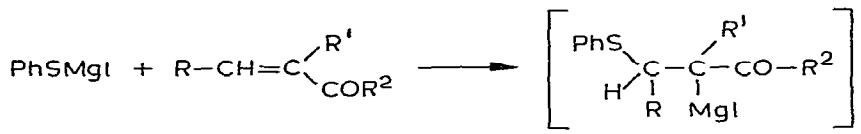
β-Ketols were prepared by the Grignard-Colonge method [207] using N-methylanilinomagnesium iodide as a base, while 2,4,6-trimethyl phenoxymagnesium bromide was utilized in the crosscondensation of α,β-unsaturated aldehydes and methyl ketones [208,209]. An α-bromo ketone was transformed into its corresponding enolate on treatment with magnesium [210].

A one-step joining reaction of thiolate anion, activated olefine and carbonyl compound was performed, which included the formation of an magnesium enolate 79 as intermediate [211].



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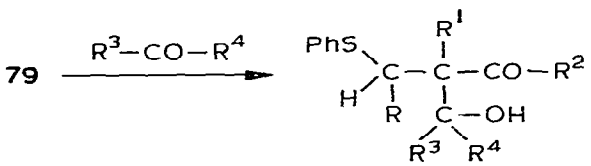


A general synthesis of 2'-hydroxychalcones from bromomagnesium phenoxides and cinnamic aldehydes was published [212]. It included as the key step the formation of a molecular complex between the magnesium phenoxide and the aldehyde which directs the aldehyde attack on the ortho position in the phenol ring.

Finally, a new anomalous Grignard reaction seemed to take place in the cyclic dimerization of sterically hindered β-methyl -α,β unsaturated ketones in the presence of Grignard reagents [213].

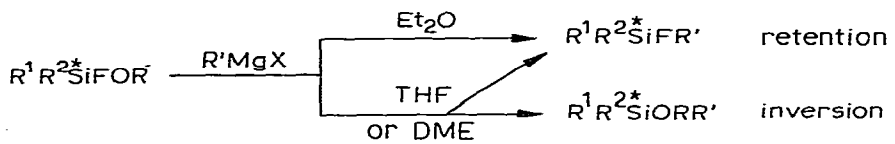
IX. OTHER REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

The first part of this chapter deals with silicon chemistry of Grignard reagents.

The reaction of vinylchlorosilanes with magnesium gave Grignard intermediates [214] $(CH_2{=}CH)_nMe_{3-n}SiMgCl$ (n = 1, 2) which were subsequently condensed with chlorosilanes.

The stereochemical behavior of chiral fluoroalkoxysilanes in

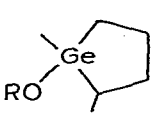
the presence of Grignard reagents was studied [215,216]. Saturated, aromatic and vinylic organomagnesium compounds reacted with $R^1R^{2*}SiFOR$ (where R = menthyl, R^1 = 1-naphthyl, R^2 = phenyl) in ether with selective and stereoselective loss of an alkoxy group and retention of configuration. The selectivity was explained in terms of electrophilic assistance of magnesium on oxygen, which governs the cleavage of the Si-O bond. When the Grignard reagent is more strongly solvated (THF or DME), competitive displacement of both fluorine and the alkoxy group was observed, the second with retention of configuration, whereas fluorine was displaced with inversion of configuration [215,216].



The reaction of phenylmagnesium bromide with $Cl_3Si(CH_2)_3Cl$, which led to the formation of $Ph_2SiCl-(CH_2)_3Cl$, was utilized in the first step of the preparation of sila-drugs [217]. The reactivity of 1,1,3,3-tetrachloro-1,3-disilacyclopentanes with RMgX was studied [218]. The reaction of $(Cl_3Si)_2CCl_2$ with methylmagnesium chloride was found to give $(Me_3Si)_2C{=}CH_2$ [219]. The mechanism of this reaction was investigated and $(Me_3Si)_2CClMe$ was regarded as a possible intermediate.

The substitution reaction of an alkoxy group by the Grignard reagents derived from para-dichlorobenzene on $(RO)_2SiMe_2$ was published [220], as well as the cleavage of siloxanes [221] and the reaction with silicon peroxides [222].

The reactions of Grignard reagents with 1,2-dimethyl 1-alkoxygermacyclopentane 80 were studied [223].

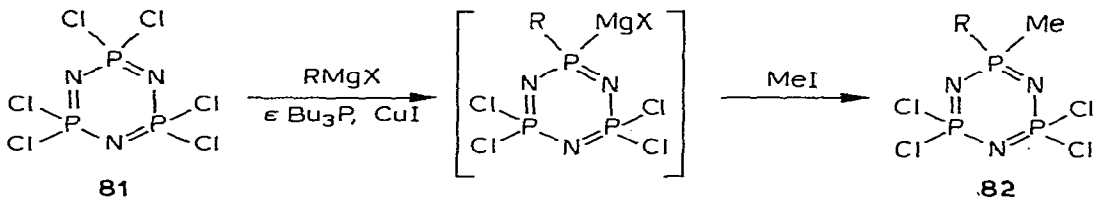


80

Tricyclohexyltin chloride was prepared from $SnCl_4$ and cyclohexyl Grignard reagents in the presence of tertiary amines [224], while tri-substituted arsenic derivatives could be obtained by coupling Ar_2AsCl with RMgX [225].

The synthesis of new gem-dialkyltetrachlorocyclophospazenes was realized via metallophosphozane intermediates [226].

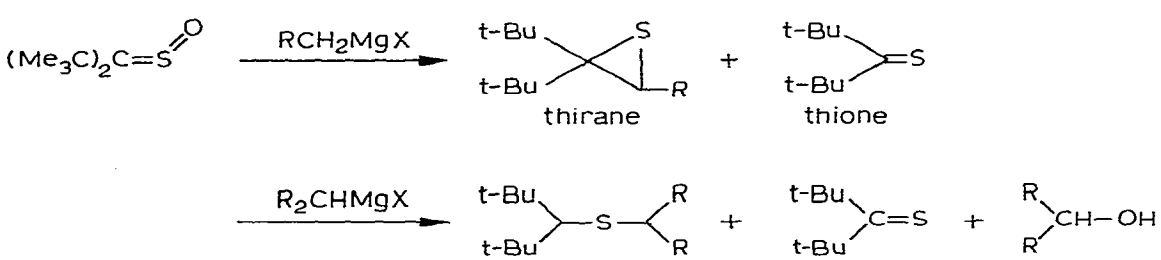
The reaction of a Grignard reagent with 81 in the presence of the Bu_3P-CuI complex was followed by addition of alkyl halides and furnished 82



81 82

The substitution of 2-chloro-5-t-butyl-1,3,2-dioxa phosphorinane and 2-chloro-3,4-dimethyl-5 phenyl-1,3,2-oxazophospholane by Grignard reagents was studied [227]. Phosphine oxides with a polyfluorinated side chain were obtained by coupling a bromomagnesium phosphine oxide, Me_2PMgBr, with iodoalkanes, $C_nF_{2n+1}CH_2CH_2I$ [228].

The reaction of $(Me_3C)_2C{=}S{=}O$ with Grignard reagents, RCH_2MgX, gave a thirane, whereas Me_3CMgCl yielded $(Me_3C)_2C{=}S$ and R_2CHMgX afforded a sulfide [230].



The reactions were interpreted in terms of competitive nucleophilic attack (primary alkylmagnesium halide) and one electron transfer (tert-alkyl magnesium halide) process).

An improved preparation of sulfinate magnesium salts was achieved by addition of an excess of SO_2 to Grignard reagents [229].

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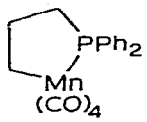
The Grignard reaction of $(CO)_5MnBr$ with $Ph_2P-(CH_2)_3MgCl$ gave 84 [231].



84

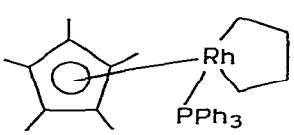
Nitro compounds, on reaction with $RCOFe(CO)_4MgBr$, gave amides [232].

$$ArNO_2 + RCOFe(CO)_4MgBr \longrightarrow RCONHAr$$

The synthesis of sigma-aryl compounds of molybdenum, rhenium ruthenium and rhodium from metal-metal bonded dinuclear acetates of molybdenum(II), rhenium(III), ruthenium(II,III) and rhodium(II) was achieved by reaction with diarylmagnesium in the presence of trimethylphosphine [233]. The reaction of $RhI_2P(Ph_3)$ (η^5C_5Me) 83 and the di Grignard reagent

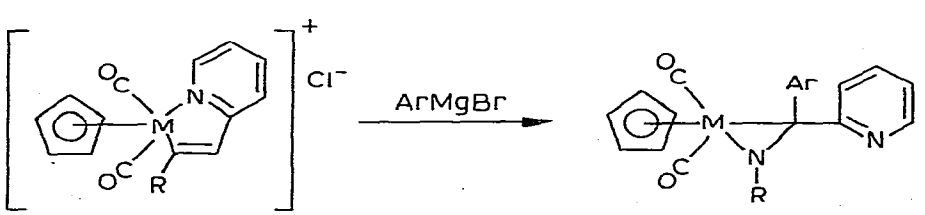
in diethylether gave a mixture of the ethylene rhodium complex $[Rh(C_2H_4)PPh_3$ ($\eta^5C_5Me_5$)] and the rhodacyclopentane 85.

In THF only, 85 was formed [234].



85

The complex 86 reacted with ArMgBr to give a metalloaziridine [235].



M = W, Mo

86

The preparation of $R_{3-n}TICl_n$ was performed by alkylation of $TICl_3$ by EtMgBr [236]. The codimerization of ethylene with isoprene and 1,3-cyclohexadiene was realized in the presence of Cp_2TiCl_2, EtMgBr or $CpTiX_2$,MeMgI [237]. The specific action of Grignard reagents on the $Al(Et)_3$, $TiCl_4$ system for the polymerization of ethylene was described [238].

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